IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	: Colbert, et al.	Art Unit	: 1754
Serial No.	: 10/670,955	Examiner	: James Fiorito
Filed	: September 25, 2003	Conf. No.	: 7093
Title	: METHOD FOR END-DERIVATIZING SINGLE-WALL CARBON NANOTUBES (AS AMENDED)		

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BRIEF ON APPEAL

This Appeal Brief is submitted pursuant to the Notice of Appeal filed in the U.S. Patent and Trademark Office on March 9, 2007, and in support of the appeal from the Final Rejection set forth in the Office Action mailed on September 11, 2006. The fee for filing a brief in support of an appeal is enclosed herewith.

I. REAL PARTY-IN-INTEREST

The real party-in-interest is William Marsh Rice University, the assignee of the entire right and interest in the present Application.

II. RELATED APPEALS AND INTERFERENCES

There are no appeals or interferences known to Appellant, the Appellant's legal representative, or assignee that will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

III. STATUS OF CLAIMS

Claims 84-85, 91-92, and 94-95 are pending in the Application.

Claims 84-85, 91-92, and 94-95 stand rejected.

Claims 84-85, 91-92, and 94-95 are being appealed.

IV. STATUS OF AMENDMENTS

There were no amendments to the claims or Specification filed after the Final Rejection.

V. SUMMARY OF THE INVENTION

The claims relate to a method for end-derivatizing single-wall carbon nanotubes. A brief explanation of single-wall carbon nanotubes is given in the Application at page 25, line 25, through page 27, line 3.

Tubular carbon molecules can be chemically derivatized at their ends (which may be made either open or closed with a hemi-fullerene dome). Application, at 34, *ll.* 11-13. Alternatively, the fullerene caps of the single-walled nanotubes (SWNT) may be removed at one or both ends of the tubes by short exposure to oxidizing conditions (*e.g.*, with nitric acid or O_2/CO_2) sufficient to open the tubes but not etch them back too far, and the resulting open tube ends may be derivatized using known reaction schemes for the reactive sites at the graphene sheet edge. *Id.*, at 34, *ll.* 17-22. Derivatives and substituents are shown on in the Application on page 34, *l.* 23 through page 37, *l.* 16.

According to one of the independent claims, Claim 84, the method for end-derivatizing single-wall carbon nanotubes in the claimed invention comprises the steps of a) providing a plurality of single-wall carbon nanotubes; and b) reacting the single-wall carbon nanotubes with a compound that provides at least one substituent on at least one of the ends of at least a portion of the single-wall carbon nanotubes.

According to another of the independent claims, Claim 91, the method for end-derivatizing single-wall carbon nanotubes in the claimed invention comprises a method for producing end-derivatized single-wall carbon nanotubes comprising the steps of a) providing a plurality of single-wall carbon nanotubes, wherein the carbon nanotubes comprise at least about 100 carbon atoms; and b) reacting the single-wall carbon nanotubes with a compound that provides at least one substituent on at least one of the ends of at least a portion of the single-wall carbon nanotubes. The method is described in the application at page 34, line 10 through page 37, line 16.

VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

A. Claims 94-95 stand rejected under 35 U.S.C. § 112, ¶ 1, as failing to comply with the written description requirement.

B. Claims 84-85, 91-92, and 94-95 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 5,698,175 to Hiura ("*Hiura*") in view of "Single-shell carbon nanotubes of 1-nm diameter," Iijima *et al.*, *Nature*, Vol. 363, pp.603-605 ("*Iijima*").

VII. ARGUMENTS

A. Claims 94 and 95 Comply With 35 U.S.C. § 112, ¶ 1

Examiner has rejected Claim 94 and 95 under 35 U.S.C. § 112, ¶ 1, as failing to comply with the written description requirement. Final Office Action, at 2.

The Examiner contends that the instant specification teaches that "[t]he ends of the single-wall carbon nanotubes are open, or closed. However, a combination of open and closed nanotubes is not taught in the specification." *Id.*

Applicant traverses these rejections.

1. Claim 94

Support for the combination of open and closed nanotubes is taught multiple times in the Application, for example, as cited below.

> Fullerene tubes may be closed at one or both ends with end caps or open at one or both ends.

Application, at 25, *ll.* 16-17.

> The nanotube can have a fullerene cap (e.g., hemispheric) at one end of the cylinder and a similar fullerene cap at the other end. One or both ends can also be open.

Id. at 33, *ll.* 24-26.

> The tubular carbon molecules (including the multiwall forms) produced as described above can be chemically derivatized at their ends (which may be made either open or closed with a hemi-fullerene dome).

Id., at 34, *ll.* 11-13.

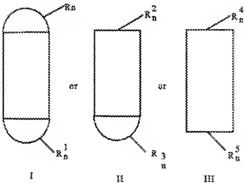
> Alternatively, the fullerene caps of the single-walled nanotubes may be removed at one or both ends of the tubes by short exposure to oxidizing

> conditions (e.g., with nitric acid or O_2/CO_2) sufficient to open the tubes but not etch them back too far, and the resulting open tube ends maybe derivatized using known reaction schemes for the reactive sites at the graphene sheet edge.

Id., at 34, *ll.* 17-22.

In addition, the combinations of end-derivatized single-wall carbon nanotubes are diagrammed, as shown below:

In general, the structure of such molecules can be shown as follows:



Id., at 34, *ll.* 23-25.

In these three molecules diagrammed in the Application and reproduced above, the vertical rectangular boxes are each a "substantially defect-free cylindrical graphene sheet (which optionally can be doped with non-carbon atoms) having from about 10^2 to about 10^6 carbon atoms, and having a length of from about 5 to about 1000 nm, preferably about 5 to about 500 nm" *i.e.*, the tube section of a single-wall carbon nanotube. *Id.*, at 35, *ll.* 6-10. Moreover, in these three molecules reproduced above, the semi-circles are each "a fullerene cap that fits perfectly on the cylindrical graphene sheet, has at least six pentagons and the remainder hexagons and typically has at least about 30 carbon atoms.," *i.e.*, an end cap of a single-wall carbon nanotube. *Id.*, at 35, *ll.* 12-15. Hence, the second molecule (II) reproduced above is a single-wall carbon nanotube with one end opened and the other end closed.

In light of the foregoing, the claimed subject matter was described in the specification in such a way as to reasonably convey such subject matter to one skilled in the art. Therefore, Claim 94 meets the written description requirement and would be understood by a person skilled in the art.

Accordingly, Claim 94 complies with the written description requirement under § 112, ¶ 1.

2. Claim 95

For the reasons discussed in Section VII.A.1 above, Claim 95 meets the written description requirement and would be understood by a person skilled in the art. Accordingly, Claim 95 also complies with the written description requirement under § 112, ¶ 1.

B. <u>35 U.S.C. § 103(a) Rejections</u>

The Examiner has rejected Claims 84-85, 91-92, and 94-95 under 35 U.S.C. § 103(a) as being unpatentable over *Hiura* in view of *Iijima*. In both the first Office Action of March 28, 2006 ("Office Action") and the Final Office Action of September 11, 2006, ("Final Office Action"), the Examiner contended that:

> *Hiura* discloses a method for producing end-derivatized carbon nanotubes comprising the steps of: a) providing a plurality of carbon nanotubes with at least about 100 carbon atoms; and b) reacting the carbon nanotubes with a compound that provides at least one substituent on at least one of the ends of least a portion of the carbon nanotubes (Abstract). At least one substituent is selected from the group consisting of alkyl; acyl; aryl; aralkyl; halogen; substituted thiol; unsubstituted thiol; substituted amino; unsubstituted amino; hydroxyl (Column 3). The derivatized carbon nanotubes are inherently soluble in some medium.

Office Action, at 3-4 and Final Office Action, at 3.

Applicant traverses these rejections.

1. Claim 84

Applicant presented arguments in reply to the Office Action and the Final Office Action in the Amendment Under 37 C.F.R. § 1.111, filed June 26, 2006 ("the 1.111 Amendment") and Amendment Under 37 C.F.R. § 1.116, filed November 13, 2006 ("the 1.116 Amendment"), respectively.

In its recent opinion in *KSR Int'l Co. v. Teleflex, Inc.*, No. 04-1350 (U.S. Apr. 30, 2007), the Supreme Court reaffirmed the *Graham* factors in the determination of obviousness under § 103. *KSR Int'l*, slip op., at 2. The four factual inquiries under *Graham* are:

(a) determining the scope and content of the prior art;

(b) ascertaining the differences between the prior art and the claims in issue;

(c) resolving the level of ordinary skill in the pertinent art; and

(d) evaluating evidence of secondary consideration.

Id. (quoting *Graham v. John Deere*, 383 U.S. 1, 17-18, 148 U.S.P.Q. 459, 467 (1966)).

The Supreme Court further noted the obviousness analysis under § 103 should be explicit, and that it was "important to identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the [prior art] elements" in the manner claimed. The Court expressly held:

> Often, it will be necessary . . . to look to interrelated teachings of multiple patents; the effects of demands known to the design community or present in the marketplace; and the background knowledge possessed by a person having ordinary skill in the art, all in order to determine whether there was an ***apparent reason*** to combine the known elements in the fashion claimed by the patent at issue. To facilitate review, this analysis ***should be made explicit***.

KSR Int'l, slip op., at 14 (emphasis added). Accordingly, when rejecting a claim based upon a combination of prior art references, it remains necessary to identify the reason why a person of ordinary skill in the art of the patent would have combined the prior art elements in the manner claimed.

Moreover, there must be a reasonable expectation of success when combining these references, which reasonable expectation must be found in the prior art and not based upon applicant's disclosure. Finally, the prior art reference (or references when combined) must teach or suggest all the claim limitations. *See* M.P.E.P. 706.02(j); *see also In re Vaeck*, 947 F.2d 488, 20 U.S.P.Q.2d 1438 (Fed. Cir. 1991).

a. There Are Crucial Differences Between *Hiura* And *Iijima* And The Claims At Issue

When performing an obviousness analysis, the scope and contents of the prior art must be determined and the differences between the prior art and the claims-in-issue must be ascertained. *KSR Int'l*, slip op., at 2; *Graham*, 383 U.S. at 17-18. In the present Application, the Examiner has acknowledged that "*Hiura* does not expressly state that the carbon nanotubes are single-wall carbon nanotubes." Office Action, at 4 and Final Office Action, at 3. The fact that the processes disclosed in *Hiura* relate to ***multi-wall*** carbon nanotubes and not single-wall carbon nanotubes is critical because there are significant differences in terms of structure, properties, and chemical reactivity between multi-wall and single-wall carbon nanotubes.

The distinction between single-wall and multi-wall carbon nanotubes is important because multi-wall carbon nanotubes are fundamentally different from single-wall carbon nanotubes. Single-wall carbon nanotubes are molecules of carbon, while multi-wall carbon nanotubes are assemblies of carbon. Single-wall carbon nanotubes have only a single layer of sp^2-hybridized carbon atoms generally arranged in hexagons and pentagons. Because of their single-layer, single-wall carbon nanotubes generally cannot support defects in growth and are more susceptible to destruction by bond breakage or reaction. In contrast, multi-wall carbon nanotubes are composed of multiple, cylindrical concentric carbon layers arranged in a nested or scrolled fashion. Because of this arrangement, the carbon shells of multi-wall carbon nanotubes can withstand wall defects, which often appear as dislocations, kinks, holes, edges on the side-wall surfaces, *etc.* Also because of their multiple layers and the interconnections between these layers, multi-wall nanotubes (in comparison to single-wall nanotubes) can withstand much more rigorous chemical processing, physical conditions, and extensive chemical bond breakage without nanotube destruction.

Single-wall carbon nanotubes "rope" together and are held tightly by van der Waals forces. As such, single-wall nanotubes are difficult to separate and disperse in other media, while multi-wall nanotubes do not share the same propensity to rope and, as such, are readily separable and dispersible. The structural differences between single-wall and multi-wall carbon nanotubes also leads to differences in physical and chemical properties, such as tensile strength, modulus, flexibility, thermal conductivity, electrical conductivity, chemical reactivity and chemical stability.

As a result of such differences, the chemistry that can be done with each species is quite different and would be unpredictable.

b. There Is No Reasonable Expectation Of Success

Hiura primarily teaches the purification of multi-wall carbon nanotubes. Such purification is carried out by reacting such nanotubes with highly oxidative acids and/or oxidation agents under reflux and/or ultrasonic conditions. This purification damages the multi-wall structures, as shown graphically in *Hiura* (Fig. 3). Application of the teachings of *Hiura* to multi-wall carbon nanotubes, typically riddled with defects, results in the breaking of carbon-carbon bonds generally at regions of defects on the walls as well as the ends. *See Hiura* at

Figure 3. However, because of their multi-wall structure, the multi-wall nanotubes can withstand attack to their wall layers and still remain intact. As would be appreciated by one of skill in the art, such bond splitting with single-wall carbon nanotubes would be expected to result in destruction of the single-wall nanotubes. Rather than expect the process of *Hiura* to succeed with single-wall carbon nanotubes, it was reasonable to believe such processes would destroy them. Hence, not only would the teachings of *Hiura* when combined with the teachings of *Iijima* not have suggested a reasonable likelihood of success as applied to single-wall carbon nanotubes, such a chemical protocol would be expected to fail to achieve the desired results.

c. The Level Of Ordinary Skill In The Pertinent Art Must Be Resolved

The third *Graham* factor is to resolve the level of ordinary skill in the pertinent art. *KSR Int'l*, slip op., at 2; *Graham*, 383 U.S. at 17-18. A person of ordinary skill in the art of the Application at the time of the invention would not reasonably have expected the process of *Hiura* would succeed for single-wall carbon nanotubes. Rather, and as noted above, a person of ordinary skill in the art would have reasonably believed the *Hiura* process would destroy the single-wall carbon nanotubes, which, in fact, was a view that was widely held by those skilled in the art well after the publication dates of *Hiura* and *Iijima*, as confirmed by Dujardin *et al.*, "Purification of Single-Shell Nanotubes," *Adv. Mater.*, **10**, No. 8, 611-613 (1998) ("*Dujardin*"), attached as Exhibit A hereto.

Dujardin notes that "[i]t was believed that purification of single-shell nanotubes based on preferential oxidation and/or separation using surfactants was much more difficult that that of [multi-shell] nanotubes." *Dujardin*, at 611. A reason for this was because "gas-phase oxidation, which yields purified multishell nanotubes, destroys the single-shell nanotubes before anything else in the sample." *Id.* Thus, at the time of the invention, a person of ordinary skill in the art would have understood that, under the teachings of *Hiura*, the multi-wall carbon nanotubes were damaged by the disclosed process and resulted in the breaking of carbon-carbon bonds generally at regions of defects on the walls and ends of the multi-wall carbon nanotubes. Such a person of ordinary skill would have further recognized that, because of the multi-wall structure of the carbon nanotubes being tested in *Hiura*, those carbon nanotubes would have withstood the attack to their wall layers and would still have remained intact. However, such person would also have

expected that the bond splitting that was occurring in the *Hiura* process would have also destroyed single-wall carbon nanotubes.

Thus, not only would have it not been obvious to one of ordinary skill in the art to apply the processes of *Hiura* to the nanotubes of *Iijima* to achieve the end-derivatization of single-wall carbon nanotubes, one of ordinary skill in the art would have been discouraged to apply the processes of *Hiura* to the nanotubes of *Iijima* because there would not be a reasonable expectation of success.

d. Examiner Must Consider The Objective Evidence

The fourth *Graham* factor is the evaluation of evidence of secondary consideration. *KSR Int'l*, slip op., at 2; *Graham*, 383 U.S. at 17-18.

i. The Examiner Did Not Properly Consider The Objective Evidence In The Office Actions

Nonetheless, it appears the Examiner ignores evidence of secondary consideration pertaining *Dujardin* and the statements made therein, because, according to Examiner, these statements apply to only gas-phase oxidation of multi-shell nanotubes. Final Office Action, at 5. This is not so. First of all, one of the authors of *Dujardin* is Prof. T. W. Ebbesen. *Dujardin*, at 611. Dr. Ebbesen is also, in fact, a named co-inventor of *Hiura*. *Hiura*, at cover page. Hence, there can be no dispute that the authors of *Dujardin* were fully cognizant of the processes disclosed in *Hiura*, when providing this statement.

However, any question as that this statement applied also to the processes disclosed in *Hiura* is completed negated by looking at the endnotes specifically in *Dujardin*. In particular, at the end of the quoted sentence in *Dujardin*, the authors referenced 4 papers, including as end note [6]. H. Hiura, T.W. Ebbesen, K. Tanigaki, *Adv. Mater.*, **1995**, 7, 275. *See Dujardin*, at 611 & 613. This reference ("*1995 Hiura*"), is entitled, "Opening and Purification of Carbon Nanotubes in High Yields," and is attached at Exhibit B hereto. This paper makes clear the authors (which included both Dr. Hidefumi Hiura, and Dr. T.W. Ebbesen, the named inventors of *Hiura*), were trying "well-known oxidants, such as nitric acid, sulfuric acid, the mixture of both and potassium permanganate" for opening and purifying multi-shelled carbon nanotubes. *1995 Hiura*, at 275. Thus, the statement made in *Dujardin* applies to liquid-phase oxidation (as well as gas-phase oxidation) of multi-shell nanotubes. And, therefore, *Dujardin* directly shows that a

person of ordinary skill in the art would not have expected, at the time of the invention, the results shown in the present Application. For that matter, this evidence clearly shows that even the inventors of *Hiura* would not have expected this result.

Examiner further asserted that the argument presented by the Applicant was "unpersuasive because the instant process is also carried out by reacting nanotubes with highly oxidative acids and/or oxidation agents under reflux conditions. Therefore, it appears that the process of *Hiura* in view of *Iijima* and the instantly claimed process would produce similar results." Final Office Action, at 4. In other words, the Examiner is relying on Applicant's own disclosure to argue that the unexpected result was expected. It is clearly in error to rely on Applicant's own disclosure in this manner, because, if this were allowed then there would never be "unexpected results" when the results of the applied for invention could be used to determine what a person of ordinary skill would have expected. In short, to protect against a hindsight analysis, the Applicant's own disclosure cannot be utilized in this manner.

Accordingly, it is impermissible to rely on the Applicant's disclosure to show the invention was expected and the Examiner cannot ignore the statements made in the art that show that a person of ordinary skill in the art would reasonably have been believed that the *Hiura* process would destroy single-wall carbon nanotubes.

Evidence of unexpected results must be considered by Examiner. M.P.E.P. § 2141; *see also In re Sernaker*, 702 F.2d 989, 996, 217 U.S.P.Q. 1, 7 (Fed. Cir. 1983). Moreover, such evidence "serve[s] as insurance against the insidious attraction of the siren hindsight" when evaluating the prior art. *W.L. Gore & Assoc. v. Garlock, Inc.*, 721 F.2d 1540, 1553, 200 U.S.P.Q. 303, 313 (Fed. Cir. 1983).

ii. The Examiner Did Not Properly Consider The Objective Evidence In The Advisory Action

In the Advisory Action having a mailing date of December 6, 2006, ("Advisory Action"), the Examiner noted that "neither preferential oxidation and/or separation using surfactants is recited in any of the instant claims.... Since the instant claims are substantially broad in nature and do not mention preferential oxidation and/or separation using surfactants, it is maintained that it would have been obvious at the time of invention to combined [*sic*] the process of Hiura

and Iijima to obtain the instant invention regardless of how 'difficult' Dujardin believed it to be." Advisory Action, at 2.

Examiner further contends that "Dujardin teaches that efforts to end derivatize single walled nanotubes were directed at modifying other techniques originally developed for multishell nanotubes. Therefore, it would have been obvious according to Dujardin to use the technique of Hiura to end derivatize single shelled nanotubes, since Hiura was a technique originally developed for multishell nanotubes." *Id.*

Regarding the Examiner's statements in the Advisory Action, Applicant believes that the Examiner is misguided in these statements.

First, regarding how "difficult" *Dujardin* believed the purification of single-shell nanotubes were, based on preferential oxidation and/or separation using surfactants versus that of multishell nanotubes, Applicant contends that there is no requirement that claims of the instant invention recite any particular type of derivatization such as preferential oxidation and/or separation.

Second, regarding the Examiner's contention that "*Dujardin* teaches that efforts to end derivatize single walled nanotubes were directed at modifying other techniques originally developed for multishell nanotubes." (*Id.*), the Examiner apparently misread the statement in *Dujardin*, which states "So efforts have been directed at modifying other techniques originally developed for multishell nanotubes." (*Dujardin* at 611, Col. 1, par. 2) The "efforts" refer to ***purification***, not ***end-derivatization***. This is substantiated by the end note references [9] and [10] in *Dujardin* that are associated with this statement and are directed at ***purification*** techniques that do not involve oxidation or derivatization of any kind. End note reference [9] refers to Tohji, *et al.*, "Purification Procedure for Single-Wall Carbon Nanotubes," *J. Phys. Chem. B* **1997**, 101, 1974-1978, ("*Tohji*"); and end note reference [10] refers to "Purification of Single-Wall Carbon Nanotubes by Microfiltration," by Bandow, et al., *J. Phys. Chem. B* **1997**, 101, 8839-8842, ("*Bandow*"). Like *Bandow*, *Tohji* does not teach any derivatization or oxidation of single-wall carbon nanotubes. *See Tohji,* attached at Exhibit C hereto.

Therefore, in light of all of the foregoing and because a *prima facie* case of obviousness has not been established for Claim 84, this Claim cannot be held obvious under 35 U.S.C. § 103(a).

2. Claim 85

For the reasons discussed in Section VII.B.1 above, a *prima facie* case of obviousness has not been established for Claim 85. Therefore, this Claim cannot be held obvious under 35 U.S.C. § 103(a).

3. Claim 91

For the reasons discussed in Section VII.B.1 above, a *prima facie* case of obviousness has not been established for Claim 91. Therefore, this Claim cannot be held obvious under 35 U.S.C. § 103(a).

4. Claim 92

For the reasons discussed in Section VII.B.1 above, a *prima facie* case of obviousness has not been established for Claim 92. Therefore, this Claim cannot be held obvious under 35 U.S.C. § 103(a).

5. Claim 94

For the reasons discussed in Section VII.B.1 above, a *prima facie* case of obviousness has not been established for Claim 94. Therefore, this Claim cannot be held obvious under 35 U.S.C. § 103(a).

6. Claim 95

For the reasons discussed in Section VII.B.1 above, a *prima facie* case of obviousness has not been established for Claim 95. Therefore, this Claim cannot be held obvious under 35 U.S.C. § 103(a).

Please apply the brief fee of $500 and any other charges or credits to Deposit Account No. 06-1050.

Respectfully submitted,

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CLAIMS APPENDIX

84. A method for producing end-derivatized single-wall carbon nanotubes comprising the steps of:

a) providing a plurality of single-wall carbon nanotubes; and

b) reacting the single-wall carbon nanotubes with a compound that provides at least one substituent on at least one of the ends of at least a portion of the single-wall carbon nanotubes.

85. The method of claim 84 wherein the at least one substituent is selected from the group consisting of alkyl; acyl; aryl; aralkyl; halogen; substituted thiol; unsubstituted thiol; substituted amino; unsubstituted amino; hydroxy; and OR', wherein R' is selected from the group consisting of alkyl, acyl, aryl, aralkyl, halogen, substituted thiol; unsubstituted thiol; substituted amino; unsubstituted amino, a linear carbon chain and a cyclic carbon chain and wherein the linear carbon chain, the cyclic carbon chain, or both are (a) optionally interrupted with one or more heteroatom and (b) optionally substituted with one or more =O, or =S, hydroxy, an aminoalkyl group, an amino acid, or a peptide of 2-8 amino acids.

91. A method for producing end-derivatized single-wall carbon nanotubes comprising the steps of:

a) providing a plurality of single-wall carbon nanotubes, wherein the carbon nanotubes comprise at least about 100 carbon atoms; and

b) reacting the single-wall carbon nanotubes with a compound that provides at least one substituent on at least one of the ends of at least a portion of the single-wall carbon

nanotubes.

92. The method of claim 91 wherein the at least one substituent is selected from the group consisting of alkyl; acyl; aryl; aralkyl; halogen; substituted thiol; unsubstituted thiol; substituted amino; unsubstituted amino; hydroxy; and OR', wherein R' is selected from the group consisting of alkyl, acyl, aryl, aralkyl, halogen, substituted thiol; unsubstituted thiol; substituted amino; unsubstituted amino, a linear carbon chain and a cyclic carbon chain and wherein the linear carbon chain, the cyclic carbon chain, or both are (a) optionally interrupted with one or more heteroatom and (b) optionally substituted with one or more =O, or =S, hydroxy, an aminoalkyl group, an amino acid, or a peptide of 2-8 amino acids.

94. The method of claim 84, wherein the ends of the single-wall carbon nanotubes are open, closed, or a combination thereof.

95. The method of claim 91, wherein the ends of the single-wall carbon nanotubes are open, closed, or a combination thereof.

EVIDENCE APPENDIX

(1) *Dujardin et al.*, "Purification of Single-Shell Nanotubes," Adv. Mater., 10, No. 8, 611-613 (1998) which was attached to the Amendment Under 37 C.F.R. § 1.111, filed June 26, 2006, of the present Application and entered by the Examiner. This paper is attached to this Brief at Exhibit A.

(2) H. Hiura, T.W. Ebbesen, K. Tanigaki, "Opening and Purification of Carbon Nanotubes in High Yields," *Adv. Mater.*, **1995**, 7, 275, which was attached to the Amendment Under 37 C.F.R. § 1.116, filed November 13, 2006 and entered by the Examiner. This paper is attached to this Brief at Exhibit B.

(3) Tohji, *et al.*, "Purification Procedure for Single-Wall Carbon Nanotubes," *J. Phys. Chem. B* **1997**, 101, 1974-1978, which was submitted in the present Application in an Information Disclosure Statement, dated February 26, 2004, Ref BTB, and considered by the Examiner on March 16 2006. This paper is attached to this Brief at Exhibit C.

No other evidence was submitted pursuant to §§1.130, 1.131, or 1.132 of 37 C.F.R. or of any other evidence entered by the Examiner and relied upon by Appellants in the Appeal.

RELATED PROCEEDINGS APPENDIX

There are no related proceedings to the current proceeding.

EXHIBIT
A

ADVANCED MATERIALS

Purification of Single-Shell Nanotubes**

By *Erik Dujardin, Thomas W. Ebbesen,* Ajit Krishnan,* and *Michael M. J. Treacy*

The recent discoveries of methods[1,2] for large-scale synthesis of single-shell nanotubes has opened the door to studying their physical and chemical properties, which are expected to be quite unique.[3,4] However, the samples still contain large amounts of impurities (typically 30 % or more), such as amorphous carbon and catalytic metal particles, that need to be eliminated for accurate measurements, whether one studies the bulk or the individual tubes. Here we report an extremely simple and efficient method for removing most of the impurities from the nanotube samples.

It was believed that purification of single-shell nanotubes based on preferential oxidation and/or separation using surfactants was much more difficult than that of multishell nanotubes.[5-8] For instance, gas-phase oxidation, which yields purified multishell nanotubes,[5] destroys the single-shell nanotubes before anything else in the sample. So efforts have been directed at modifying other techniques originally developed for multishell nanotubes.[9,10] Tohji et al.[9] published a method using ultrasonication in water and treatment with hydrochloric acid. The yield of pure single-shell nanotubes is only 3 % of the starting material for a 48 h process. More recently, Bandow et al.[10] reported a method mainly based on microfiltration under overpressure. A major advantage of this process is that it is driven by pure physicochemical interactions of the carbon products with the amphiphilic molecules and the filter membrane, leaving the nanotubes undamaged. The most serious drawback is the dependence of this procedure on the quality of the sample. It is known that sonicating nanotubes for a long period of time and at a high frequency can cause damage by breaking the nanotubes up into smaller pieces.[11] We have found it hard to successfully apply this method to all samples. Typically, significant amounts of amorphous carbon and catalytic particles remain.

The one-step method presented here does not appear to be sensitive to the quality of the starting material. Moreover, it eliminates at the same time the carbonaceous material and most of the catalytic metal content.

The single-shell nanotubes were prepared by the laser-oven ablation method[1] (see Experimental section). In this way, up to 30 mg/h of raw material could be synthesized, providing that the focused laser spot was continuously moved on the target surface to uniformly ablate the superficial material. Among all the parameters of this method, this one seems to be the most critical in order to obtain good yields. The transmission electron microscopy (TEM) pictures in Figure 1 show the quality of such raw single-shell nanotube samples. Typically, there is a mixture of ca. 50 % of bundles of single-shell nanotubes and ca. 50 % of carbonaceous material, gray graphitic nanoparticles, and black catalyst (cobalt and nickel) grains (Fig. 1a). A closer examination (Fig. 1b) of the tubes shows a layer of irregular thickness of amorphous carbon coating the bundles, which is particularly abundant where the bundles cross.

In the desire to open single-shell nanotubes with acids, we processed the raw nanotube samples in boiling concentrated nitric acid (See Experimental section). This method was developed for opening and filling multishell nanotubes by Green and co-workers.[7] To our surprise, the nanotube sample seemed to become purer. After refluxing the sample for

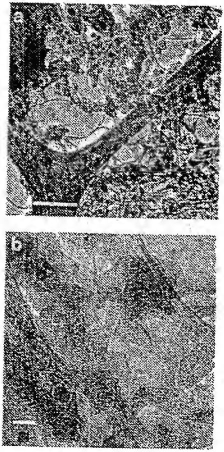

Fig. 1. TEM micrographs at low (a, scale bar 0.2 μm) and high (b, scale bar 20 nm) magnification of as synthesized single-shell nanotubes. Microscope Hitachi H9000-NAR, 300 kV.

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4 h in 70 % nitric acid at 120 °C, it was pure. The result of such a treatment is shown in Figures 2a and 2b. It is striking that the single-shell nanotubes appeared to be sufficiently (chemically) inert for a large proportion to survive such strongly oxidizing conditions. The yields, in terms of left-over weight of the sample after oxidation, can be as high as 50 %, which appears to reflect the initial nanotube content.

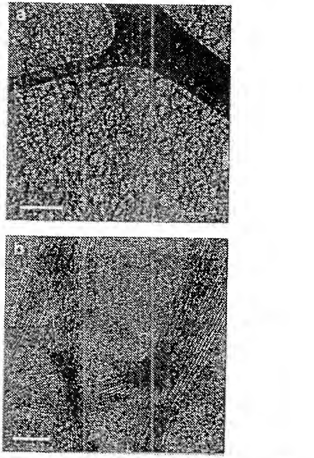

Fig. 2. TEM micrographs at low (a, scale bar 0.2 mm) and high (b, scale bar 20 nm) magnification of as-synthesized single-shell nanotubes purified by treatment in boiling nitric acid. Microscope Hitachi H9000-NAR, 100 kV. Note: The treated samples are more sensitive to the TEM beam than the original material, probably due to the presence of the oxides.

Large areas of the mat formed by the pure single-shell nanotubes on the TEM grids revealed no severe damage to the walls of the nanotubes, as shown in Figure 2b. The nitric acid not only reacts preferably with the particles but it leaves most of the tubes intact in the bundles. Occasionally one can see isolated tubes but it is very difficult to tell whether the tubes are open or not because of the low contrast of a single carbon wall. Some debris can still be seen on the outside of the bundles. Probably, after removing the impurities, the acid reacts with the outermost tubes of the bundles. In other words, the outer tubes in the bundle protect the inner ones.

In this regard, it should also be noted that no distortion or loss of contrast is visible in the TEM pictures of the walls of the single-shell nanotubes in the purified samples. This could mean that the sp^2 structure is mostly conserved and that the amount of sp^3 carbons bearing alcohol, carboxylic or carbonyl functions is quite small. This is unlike multishell nanotubes, where these functional groups are found to cover the entire surface.[6] Nevertheless, those hydrophilic groups are undoubtedly present on the purified single-shell nanotubes since the purified nanotubes are much more stable in aqueous suspensions than the raw ones. Like multishell tubes, annealing of the samples at high temperature should eliminate residual surface oxides.[17]

Although we did not see any remaining catalytic particles in the sample, a chemical analysis was performed on the samples to quantify the amount of metal before and after purification. Interestingly, while the target contained 2 % metal (Ni and Co, total weight percent), the amount in the raw nanotube samples was 3 %. In terms of nanotube content this about 6 %, while purification leaves ca. 1 %. In other words, the metal content is reduced by a factor of six relative to the nanotube content. The 1% is still surprisingly large considering that these metals readily dissolve in the acid. We are currently trying to find ways of removing the remaining metal.

A final remark is warranted. Due to their high curvature, nanotubes pick up impurities from just standing in air or in a solvent. This can be a very fast process, occurring in a day or even less, depending on the environment. It results in the nanotubes being coated with a sheath of amorphous material, which is easily observed by TEM. Needless to say this can have significant consequences on any property measurements.

It seems clear from this study that the kinetics of the reactivity of single-shell nanotubes is different from that of both multishell nanotubes and fullerenes. In particular they are relatively inert toward oxidation by acids, at least in a bundle form. This property allows the purification of the as-synthesized mixture by this fast, high-yield, and easy to handle procedure. This is by far the simplest and most reproducible method to date for both single and multishell tubes. It should be a helpful step for further physical or chemical experiments and technological applications.

Experimental

Purification Processes: 10 mg of raw material (0.83 mmol of carbon) containing 40–60 % of single-shell nanotubes are sonicated in 5 mL of concentrated nitric acid (70 vol. %, 87.8 mmol) with a regular monofrequency ultrasonic bath (maximum power) for a few minutes. The suspension is then refluxed under magnetic stirring at 120–130 °C for 4 h. Dense yellow vapors of nitrogen dioxide evolve during the first 3 h, indicating a high rate of oxidation of hydrocarbons into alcohols, carboxylic acids, ketones, or aldehydes, and of metallic particles of cobalt and nickel into their corresponding ions. Later, the vapors become less dense as the nitric acid probably oxidizes less-reactive species.

The suspension is then cooled and centrifuged in glass tubes at 3400 rpm for 15 min, and the resulting yellow-brown solution is decanted. The wet powder is washed with portions of 10 mL of distilled water, centrifuged (3400 rpm, 15 min) and decanted iteratively as long as the solid settles down completely in 15 min (in general two or three washing cycles). The

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ADVANCED MATERIALS

pH of the successive washing solutions is monitored and is about six when the suspension of single-shell nanotubes starts to be stable on the centrifugation timescale. At this point, the powder is washed twice with 15 mL portions of nitric acid and filtered on fritted glass before rinsing twice with 15 mL portions of distilled water. Between each of these steps the suspension is sonicated. Finally, the wet powder is dried and kept in a dessicator under vacuum. The overall yield ranges between 30 and 50 %.

Synthesis of Single-Shell Nanotubes: A carbon target is made by mixing 31 g of graphite cement (Dylon Industries Inc.) with 2.70 g of graphite powder (GP-G, Dylon Industries Inc.), 0.35 g of cobalt (Aldrich, powder, <2 µm, 99.8 %), and 0.36 g of nickel (Aldrich, powder, submicrometer, 99.8 %). The homogeneous mixture containing 0.3 at.-% of each catalyst is molded in a 0.75 inch quartz tube (1 inch = 2.54 cm) and baked in air for 12 h at 120 °C and for 12 h at 200 °C. The baked target is then cured at 1200 °C for 6 h in vacuum (6×10^{-7} torr). For the nanotube synthesis, the target is placed in a 1 inch quartz tube under a pressure of 500 torr of argon and a gas flow of 400 cm^3/min after several purges. The quartz tube is maintained at 1200 °C during the synthesis. A YAG-Nd laser (SEO Titan-P, 10 Hz, 250 mJ/pulse at 532 nm, 250 mJ/pulse at 1064 nm) was used to generate pulsed beams at 1064 and 532 nm. The former is delayed by 15 ns with respect to the latter. Both beams are focused to a 3–4 mm spot on the target. For optimal yield, the focal spot of the beams is moved on the target every few minutes. After the synthesis runs, the quartz tube is cooled down to room temperature under argon flow. A fine web-like deposit then collects on the walls of the quartz tube and on the cold finger that closes this tube.

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EXHIBIT
B

Communications

Opening and Purification of Carbon Nanotubes in High Yields[**]

Hidefumi Hiura, Thomas W. Ebbesen,* and *Katsumi Tanigaki*

Carbon nanotubes can be thought of as cylindrical graphitic micro-crystals with nanometer diameters which are expected to have unique properties.[1] Currently multi-shell nanotubes can be made in gram-orders using the carbon arc discharge synthesis method.[2, 3] However, the crude sample contains not only nanotubes but also nanoparticles with a weight ratio of about 2:1 in the best cases. Therefore the nanotubes must be further purified in order to investigate precisely their properties.

Recently we reported the purification of nanotubes by oxidation in air at high temperature (around 750 °C).[4] In this process the nanoparticles are consumed more rapidly than the nanotubes. However the yields are very small (< 1 %) probably due to the local inhomogeneities in the gas phase oxidation process. To overcome this problem, we have investigated the liquid-phase oxidation of the crude nanotube samples and found that under suitable conditions high yields of opened purified nanotubes can be obtained.

In this paper we describe this method which gives yields of the order of 40 % depending on the composition of the crude sample. This method is very useful to obtain gram-quantities of purified nanotubes at one time under well-controlled conditions.

By analogy with the gas-phase oxidation referred to earlier,[4] we tried several well-known strong oxidants, such as nitric acid, sulfuric acid, the mixture of both and potassium permanganate. Transmission electron microscopy (TEM) observation revealed that the oxidation was much more homogeneous in solution where the nanotube sample could be well dispersed through sonication and the chemical attack could be uniform. The oxidation by sulfuric and nitric acids is extremely slow and weak. A mixture of the two gives slightly better results.

For purification purposes, by far the best oxidant is potassium permanganate in acidic solution. Therefore, for the latter case, the methodology will be described in detail next. 1.00 g of the core fibrous material is taken from the deposit synthesized by the carbon arc discharge method,[2, 3] ground and dispersed in 200 ml of 1 N sulfuric acid. This solution is placed in a two necked flask fitted with a reflux condenser. Separately, 19.8 g (1.5 molar excess in terms of atomic carbon content) of potassium permanganate is dissolved in 200 ml of 1N sulfuric acid and placed in a funnel fitted to the side neck of the flask. The flask is heated to 150 °C in an oil bath with vigorous stirring (magnetic stirrer). The potassium permanganate solution is then added drop by drop through the side funnel. The solution is then refluxed for an additional 5 hours. The mixture is then cooled and filtered through a G4 glass filter (pore size 10–16 mm). The filtrate is washed with pure water and then with concentrated hydrochloric acid to remove the manganese(IV) oxide (reduced from the original potassium permanganate). When all the manganese oxide has been dissolved away, the filtrate is again washed with pure water. The residual filtrate containing the purified nanotubes is collected and dried under vacuum for several hours.

The yield of the purified nanotubes is about 40 % in terms of the total weight of the starting raw material. Figure 1 shows the TEM pictures of the sample before and after this

Fig. 1. Carbon nanotubes before (a) and after (b) liquid phase purification.

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[**] We thank M. M. J. Treacy and M. E. Bisher for the micro X-ray analysis of the sample. Since submission of this manuscript, a method for opening nanotubes by nitric acid has been reported (Tsang et al., *Nature* 1994, 372, 159) and also confirming that nanotubes are wet by low surface tension liquids such as solvents as predicted in [7].

process. As can bee seen the nanoparticles have been removed. Sometimes some new impurities appear in the sample due to the numerous steps in the process. Micro X-ray analysis indicates one impurity is composed of silicon. This is most likely due to the etching of the glass flask by the boiling sulfuric acid and potassium permanganate mixture. This should be easily removed by treating the sample with HF or using a different container. The maximum yield cannot be higher than the amount of nanotubes in the original crude sample. Therefore the necessary excess of potassium permanganate with respect to the starting material must be calibrated to the weight ratio of nanoparticles to nanotubes in the sample.

In our case, TEM observations revealed that when the molar ratio is around 0.2, the nanotubes begin to opened and the nanoparticles become round due to reaction at the edges. When the molar ratio is about 1.5, the nanotubes are purified. However if the excess is further increased (e.g. 2.2), the nanotubes become shortened due to the excessive oxidation. The shortening is due to the fact that oxidation starts at the tips of the nanotubes as has been shown elsewhere.[3,6] This is mostly due to strain at the tip which enhance its reaction rate.[1]

The purification process therefore also opens the nanotubes on a large scale. This will be useful for doing nanoscale experiments in the hollow cavities of the nanotubes since we have shown elsewhere that they are wettable by low surface tension liquids.[7] The oxidation process changes the chemical make-up of the reactive edge of the tips and perhaps even the outer (and the inner) layer of the nanotube. This in turn might affect their properties. To check for any significant chemical modification, the purified nanotubes were analyzed by XPS (ESCA). The detailed results of the XPS analysis will be described elsewhere.[8]

Figure 2 shows the peak-separated difference XPS spectrum of the purified nanotubes around 285 eV. The main

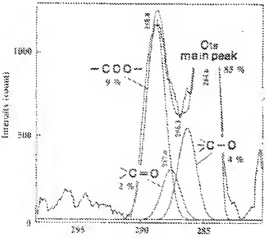

Fig. 2. The peak-separated XPS spectrum of the purified nanotubes around 285 eV. The weight percent of each of the chemical groups present are indicated.

peak (cut off) at 284.6 eV is unambiguously assigned to the C1s of graphitic carbon. The shoulder of the main peak is composed of three peaks, which are assigned to the C1s of hydroxyl carbon (286.3 eV), that of carbonyl carbon (287.6 eV) and that of carboxyl carbon (288.8 eV). The analysis of the peak areas indicates that ca. 15 percent of the carbon constituting the nanotubes are bound to those groups as indicated in Figure 2. Clearly, not only the tips but also the surface of the outer layer is covered with these species. The presence of these hydrophilic group is noticeable in that the purified nanotubes disperse much more easily in water than the original sample.

In conclusion, we have presented a simple method to obtain opened and purified nanotubes in high yields which should allow for their accurate physical characterization. With the resultant higher dispersibility, this method also opens the way for further chemical decoration and modification of carbon nanotubes and their eventual use in biomimetic systems.

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Photoconductivity in the Columnar Phases of a Glassy Discotic Twin**

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The electronic charge-carrier mobilities of organic systems are mainly determined by the supramolecular arrangement and packing of the molecular units involved. The overlap of molecular wavefunctions is often more important than the

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EXHIBIT
C

Purification Procedure for Single-Walled Nanotubes

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A purification procedure for single-walled nanotubes is presented in this report. A novel purification method that incorporates the hydrothermal treatment along with other treatments such as extraction of fullerenes and oxidation and dissolution of metal particles is used in this study. The effects of each treatment in the purification process is also discussed by characterizing the intermediate products using X-ray diffraction, Raman spectroscopy, scanning electron microscopy, and transmission electron microscopy.

Introduction

Since the discovery of single-walled nanotubes (SWNTs),[1–3] various methods for their synthesis and possible characterization have been hotly pursued.[4–16] Parallel to these efforts, theoreticians have introduced a new coordinate system to define their chiral crystallography, while others have predicted them to be one-dimensional conductors or semiconductors.[17,18] Recently, SWNTs have been successfully synthesized in large quantities using composite consumable carbon electrodes mixed with several metallic species, predominantly transition metals such as Ni, Fe, and Co.[5,6,8,16] The SWNTs synthesized by this method coexist with metals and various forms of carbon and other such impurities, resulting in a serious impediment to detailed characterization of the nanotubes and assessment of their potential utility.

In our previous report,[19] we briefly presented the novel purification method for SWNTs incorporating the hydrothermal treatment along with other treatments for the extraction of fullerene and oxidation and dissolution of metal particles. As a result, at least 20 mg of SWNTs with 95 wt % purity is obtained from 1 g of raw soot. In the hydrothermal treatment (hydrothermally initiated dynamic extraction method or HIDE),[20,21] it is believed that H_2O molecules break the network between SWNTs and amorphous carbon and metal particles and makes a valuable contribution to the overall performance of the purification process. The byproducts that coexist with SWNTs in the soot are removed at each step of the purification process. In this report, the purification procedure for SWNTs is presented and the effects of each treatment in the purification process is discussed by characterizing the intermediate products using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Experimental Section

Preparation of SWNTs. The method employed to synthesis SWNTs is the same as that employed to synthesize for nanocapsules stuffed with metal crystallites.[22–24] Packed graphite rods containing a mixture of Fe and Ni powders of 99.9% purity (Wako Chemical Co. Ltd., Japan) were used as the anode of DC arc discharge. The mixing ratio of Ni, Fe, and graphite powder for efficient production of SWNTs was roughly 1:1:3 by weight. Total metal content in the anode is approximately 6 at. %. A hole of 3.2 mm diameter and 50 mm in depth was drilled out from a graphite rod (99.998% purity, 100 mm long and 6 mm in diameter) supplied from Toshiba Ceramics Co. Ltd., Japan, and filled with a mixture of metal and graphite powders. A pure graphite rod of 10 mm in diameter was used as cathode. The arc discharge was carried out under a He atmosphere of 100 Torr. The discharge current was 70 A, and during the discharge, the gap between the electrodes was maintained at about 1 mm by manually advancing the consumed anode.

Purification of SWNTs. The soot produced by DC arc discharge was retrieved from the upper wall of the arc discharge chamber and homogenized. In the HIDE treatment, used as the initial step of the purification process, 100 mg of the soot containing SWNTs was introduced into a flask with a reflux attachment together with 50 mL of distilled water and was heated at 373 K for 12 h. The soot was disintegrated to submicron-sized particles. The processed soot was filtered and dried at 333 K for 12 h. Then, fullerenes were washed out using toluene in a Soxhlet. The residual soot was heated at 743 K for 20 min. In the final step of the purification process, the soot was treated in 6 M hydrochloric acid and almost all the metal complexes were washed out.

Evaluation of the Purification Procedure and Characterization of Purified SWNTs. The purification procedure of SWNTs was probed by SEM and XRD. The purified SWNTs were characterized by TEM and Raman scattering and their surface areas were measured by BET method. The intermediate product at each purification step was dispersed in ethanol, sonicated for 5 min, deposited on a sample stage, and observed in a SEM operated at 5 keV. XRD patterns were taken by a powder X-ray diffractometer with a Cu Kα X-ray source. For TEM observation, the sample was ultrasonically dispersed in ethanol and the suspension was dropped onto a microgrid. The Raman scattering measurements were carried out at room

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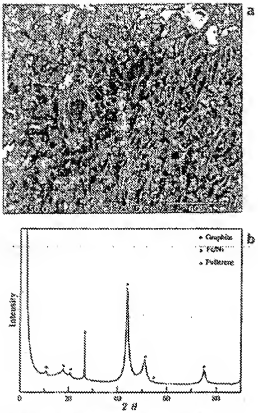

Figure 1. (Top) SEM photograph and (bottom) XRD profile of the raw soot.

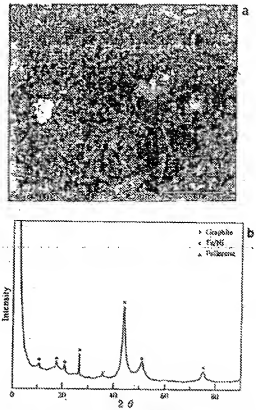

Figure 2. (Top) SEM photograph and (bottom) XRD profile of hydrothermally treated soot.

temperature using Ar ion laser (488.0 nm) in a backscattering configuration. The surface area of SWNTs was obtained from the N_2 gas adsorption isotherm equilibrium proposed by Langmuir. The amount of residual metals in the purified SWNTs was also estimated by chemical analysis using the inductively coupled plasma method (ICP).

Results and Discussion

Purification Procedure for SWNTs. In the raw soot produced by arc discharge, SWNTs coexist with many byproducts such as metal particles, fullerenes, and amorphous carbon.[5,6,8] Therefore, SWNTs have to be separated step by step in the purification processes.

Figure 1 shows the SEM photograph and XRD profile of the raw soot. Under the present preparative conditions, the SWNTs are efficiently grown and coexist with many byproducts as seen in Figure 1a. Furthermore, the SWNTs and metal particles are surrounded by carbon materials such as amorphous carbon and fullerenes. XRD pattern in Figure 1b shows the presence of C_{60}, graphite, and metal particles.

Figure 2a shows a SEM photograph of the soot treated by the HIDE method. The SWNTs certainly look much more slender in comparison to those observed in Figure 1a. The XRD profile of Figure 2b does not show any change, except for the decrease in the intensity of the 002 peak of graphite compared to that of the 002 peak in Figure 1b. This suggests that the graphite particles and amorphous carbon adsorbed on SWNTs were partly removed as a result of the HIDE treatment.

The soot used in these experiments contained about 10 wt % of fullerene. It is well-known that fullerenes can be extracted with organic solvent such as toluene, benzene, or CS_2. It has been confirmed that fullerenes are freed from the soot and extracted easily in toluene in a Soxhlet by carrying out the HIDE treatment prior to the extraction by organic solvent.[20,21] During Soxhlet extraction, in addition to the dissolution of fullerenes in toluene, the hydrophobic graphite particles are dispersed and removed from the soot.

After the above treatments, the residual soot was left only with SWNTs and metal particles wrapped with a thick amorphous carbon layer. The metal particles barely dissolved in acid. Therefore, the residual soot was baked at 743 K in air for 20 min to remove the amorphous carbon particles and the graphitic layer around the metal particles and to make them dissolve easily in acid. As a result of baking, the weight of the soot decreased by about 40%. Figures 3b,c. are the expanded portions of the left and right part of Figure 3a. As seen in Figure 3, SWNTs and metal particles formed into separate aggregates during the course of baking. The XRD profile of the baked soot shown in Figure 4 suggests that the metal particles changed to their oxides NiO and α-Fe_2O_3. At the same time, remaining amorphous carbon in the soot was burned out. It is believed that, as a result of transformation of metal alloy into metal oxides and the removal of amorphous carbon, SWNTs and metal particles are isolated from each other and form separate aggregates. However, the increase in the intensity of the graphite peak at 002 is believed due to the increase in the ratio of the graphite particles in the sample as the result of the

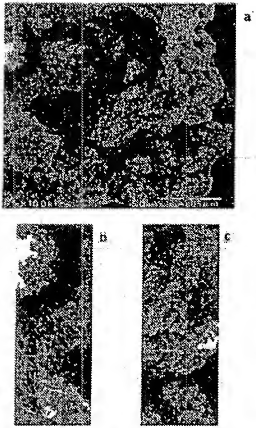

Figure 3. (Top) SEM photograph of the soot that has been hydrothermally treated, toluene extracted, and baked at 743 K. (Bottom left) and (bottom right) are the expanded portions of the left and right side of (top), respectively.

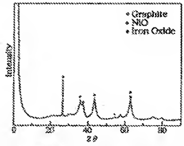

Figure 4. X-ray diffraction profile of the soot used in Figure 3.

elimination of amorphous carbon on the baking treatment. This problem is overcome by repeating the HIDE treatment and by washing with toluene. With the final treatment using 6 M hydrochloric acid, almost all the metal particles which formed into separate aggregates are washed out.

Purity of Separated SWNTs. Figures 5a,b show that high purity SWNTs are separated in large quantities. However, if we carefully observe the SEM photographs, we could find white dots of about 20 nm in diameter. To investigate this in detail, the sample used for the SEM observation was checked by high resolution TEM measurements. Figure 6a shows the TEM photograph of the portion where many metal particles exist. From the photograph, it can be seen that the particles are

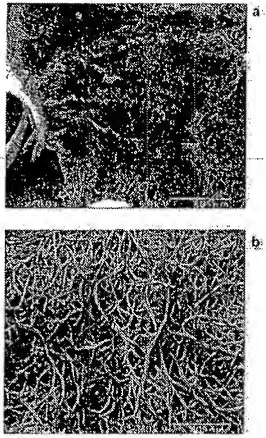

Figure 5. SEM photographs of the purified SWNTs observed under different magnifications.

nanocapsules wrapped in graphitic carbon layers. However, almost all the nanocapsules observed in Figure 6a were empty and free of metal particles. In the final product, metallic alloy particles that are perfectly covered with the graphitic layers and protected from dissolution on acid are present in very small quantities. The Ni and Fe metal concentrations in the separated SWNTs, estimated using ICP, were 2.3 and 2.5 wt %, respectively. Therefore, the purity of the separated SWNTs in this experiment is about 95 wt % while not taking the empty capsules with graphitic layers into account. Therefore, to obtain purity of over 99 wt %, these SWNTs were sonicated in water until nanocapsules were eliminated from the sample.

As seen in the TEM photograph in our previous report,[19] the other forms carbon materials were completely removed from the SWNTs. This was further confirmed by carrying out Raman scattering on a bulk sample of SWNTs. The SWNTs show multiple split Raman peaks of crystalline graphite centered at 1580 cm^{-1} because of their cylindrical symmetry.[25] Kasuya et al. have reported that the scattering wavenumber would directly provide information on SWNTs such as the tube diameter and the carbon network.[26,27] As stated in our previous report,[19] the Raman scattering from the purified SWNTs shows multiple split peaks(1570 and 1590 cm^{-1}) which are five times more intensive than those of the SWNTs in the raw soot without any change in their position and intensity ratios. From the results of Raman scattering measurements, the following can be said: (a) only trace amounts of carbon material other than SWNTs are present

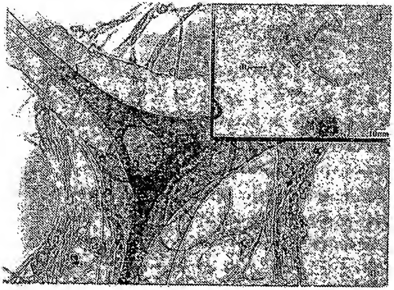

Figure 6. (a) TEM photograph of the metal particles encapsulated within the graphitic layers, which are present as impurities in the purified SWNTs. (b) A magnified portion of nanoparticles in (a).

in the final product and (b) the SWNTs have not suffered significant damage in the course of the purification procedure used.

The measurement of a specific surface area also confirms the purity of separated SWMTs. The specific surface areas of purified SWNTs, of raw soot containing SWNTs, and of fullerene soot made from pure graphite rod were 550, 170, and 110 m^2/g, respectively. For fullerene soot, the estimated average particle size assuming the density of the soot to be 2.3 g/cm^3, was 25 nm in diameter. However, the calculated average diameter of the purified SWNTs, assuming a density of 1.5 g/cm^3, was about 5 nm. This value suggests that SWNTs are contained in bundles with each made up of a few SWNTs as seen in the TEM photograph of Figure 6b.

Effects of Hydrothermal Treatment on the Purification of SWNTs. A portion of Figure 6a, in which many metal particles exist, is magnified and shown in Figure 6b. There are many nanocapsules that have received damage on the graphitic layers (for example, A in Figure 6b). Especially, the graphitic layers of some empty capsules are completely destroyed (for example, B in Figure 6b). The graphitic layers of nanocapsules are made up of small domains of graphitic carbon sheets stacked parallel to the surface of the core metal particles. Hence, the graphitic sheets of the nanocapsules, for the most part, have defects and dislocations, in contrast to the SWNTs.[28] Therefore, it is believed that the reaction of H_2O with the carbon breaks the graphitic layers that wrap the metal particles. Consequently, incorporating the HIDE treatment in the purification procedure makes possible the exposure and dissolution of the encapsulated metal particles to hydrochloric acid in the final step of the treatment.

The application of the baking technique[29] was not successful on the purification of SWNTs,[30] even though the purification of multiwalled nanotubes is possible. In the case of the baking method, graphite particles, nanocapsules, and amorphous carbon adsorbed on the SWNTs are not removed from the soot. In contrast, we believe that, during the HIDE treatment, water molecules break the network between SWNTs and amorphous carbon and metal particles and also attack the graphitic layer encapsulating the metal particles. Consequently, almost all graphite nanoparticles and nanocapsules are washed out from the soot.

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